(54) Title: POLY(PERFLUOROETHER)ACYL PEROXIDES

(57) Abstract

This invention concerns novel polymeric perfluoroether acyl peroxides and an improved process for making them.

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TITLE
POLY(PERFLUOROETHER)ACYL PEROXIDES

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BACKGROUND OF THE INVENTION
1.   Field of the Invention

This invention concerns polymeric perfluoro-
etheracyl peroxides, and an improved process for
10   making them.

Selected high molecular weight fluorocarbon and
perfluoroether peroxides have been known in the art
for a number of years. The synthesis of these
compounds has generally involved the reaction of
15   aqueous peroxide with an acid halide. Using this
method, some of the acid halide is converted to
carboxylate salt. As the molecular weight of the
carboxylate salt increases, soaps and stiff
emulsified gels are formed that interfere with the
20   isolation of the pure compound. Conventional methods
of isolating the peroxide have involved treatment of
the mixture with sulfuric acid and following up the
procedure with centrifugation to separate out the
peroxide. See, e.g., U.S. Patent 3,882,193. The
25   present invention improves upon prior art procedures
for synthesizing oligomeric peroxides by limiting the
presence of water so as to retard emulsion and gel
formation and result in the direct formation of a
liquid product containing the high molecular weight
30   perfluoroether peroxides. This invention also
concerns novel polymeric peroxides produced by the
present process, and a novel method of coating
substrates with fluoropolymers using the polymeric
peroxides.

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2.   Discussion of the Prior Art

U.S. Patents 2,559,630 and 2,792,423 disclose
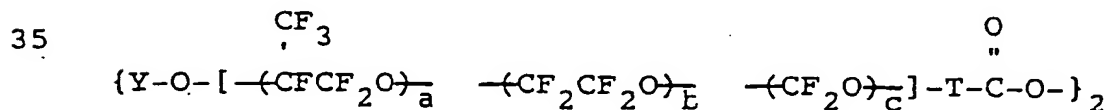polymeric perfluoroalkylacyl peroxides and a method

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for making them. The chemistry used in the process
to produce the acyl peroxides is the reaction of the
corresponding acyl halide (usually fluoride or
chloride) with a peroxide unde basic conditions.
The peroxide can be added as hydrogen peroxide and a
base such as sodium hydroxide added, or the base and
peroxide can be combined in one compound such as
sodium peroxide. The reaction is often done in a
heterogeneous system containing water to dissolve the
inorganic salts, and an organic solvent to dissolve
the perfluoro polymer.

U.S. Patents 3,810,875 and 3,882,193 disclose
polymeric perfluoroether acyl peroxides wherein both
ends of the perfluoroether polymers end in peroxides,
and each "block" of perfluoroether polymer is part of
a larger polymer molecule joined by peroxide
linkages. Thus, such poly(perfluoroether)acyl
peroxides are "difunctional", that is reactive on
both ends of the perfluoroether blocks. The same
basic chemistry described above was used to prepare
the peroxides.

Z. Chengxue et al., in Journal of Organic
Chemistry, vol. 1982, pages 2009-2013 describe the
decomposition of perfluoroacyl peroxides for both
perfluorocarbon and perfluoroether compounds, but the
molecular weights of the perfluoro segments are very
low.

SUMMARY OF THE INVENTION

A poly(perfluoroether)acyl peroxide of the
formula

$$\{Y-O-[-(\overset{CF_3}{\overset{|}{CFCF_2}}O)_a \quad -(CF_2CF_2O)_b \quad -(CF_2O)_c]-T-\overset{O}{\overset{\|}{C}}-O-\}_2$$

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wherein

    Y is a perfluoroalkyl group containing up to 12
carbon atoms, a+b+c is a minimum of 2 and a
maximum such that the maximum molecular
weight of the peroxide is about 33,000; and
    T is $-CF_2-$ and $-CF(CF_3)-$,

provided that when a is zero, T is not $-CF(CF_3)-$,
when b is zero T is not $-CF_2-$, and further provided
that when a and b are both zero, T is $-CF_2-$.

    Also provided is an improved process for the
preparation of such peroxides from the corresponding
poly(perfluoroether)acyl halide, peroxide and base,
the improvement consisting of using a specified
amount of water in the reaction. The molar ratio of
water/peroxide (starting material) present in the
reaction ranges from about 0.2 to about 10. An
optional improvement consists of passing the reaction
mixture at the conclusion of the reaction through a
solid desiccant to remove liquid water.

    Also provided is a process for the coating of
substrates with fluoropolymers using such peroxides
as the initiators. The peroxide is coated on the
substrate, as by evaporation of a solution of the
peroxide on the substrate, and then the peroxide
coated substrate is exposed to fluorine containing
monomers capable of being polymerized by free
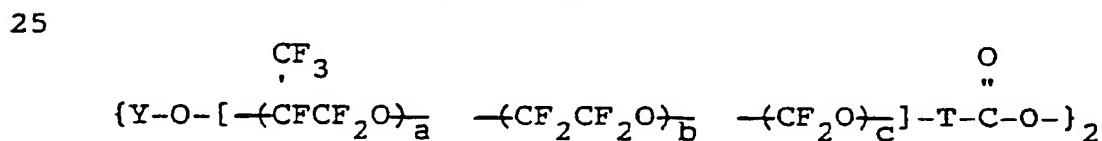radicals, at a temperature at which the peroxide
decomposes.

DETAILS OF THE INVENTION

    It is known that poly(perfluoroethers) tend to
be liquids, and it is the object of this invention to
provide liquid, easily used, poly(perfluoroether)acyl

peroxides that can be used, for example, to place
relatively large poly(perfluoroether) groups (blocks)
5   on the ends of free radical polymerized polymers.
Poly(perfluoroether)acyl peroxides are commonly
made by reacting a poly(perfluoroether)acyl halide,
usually the fluoride or chloride, with an inorganic
peroxide in the presence of base. This is usually
10   done in the presence of water, to dissolve the
inorganic reagents, and an organic solvent, to
dissolve the poly(perfluoroether)acyl halide. An
inevitable consequence of this reaction is the
production of at least small amounts of
15   poly(perfluoroether) carboxylate. When the
perfluoroether chain is of substantial length, this
acts as a surfactant, causing the formation of
virtually intractable emulsions and suspensions,
which greatly complicates isolation of the peroxide
20   and reduces the yield obtained. It is a further
objective of this invention to provide a process for
making such peroxides.
The poly(perfluoroether)acyl peroxides of this
invention have the formula
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$$\{Y-O-[-(\overset{\overset{\displaystyle CF_3}{|}}{CFCF_2O})_a \quad -(CF_2CF_2O)_b \quad -(CF_2O)_c]-T-\overset{\overset{\displaystyle O}{\|}}{C}-O-\}_2$$

wherein
30   Y is a perfluoroalkyl group containing up to 12
carbon atoms, a+b+c is a minimum of 2 and a
maximum such that the maximum molecular
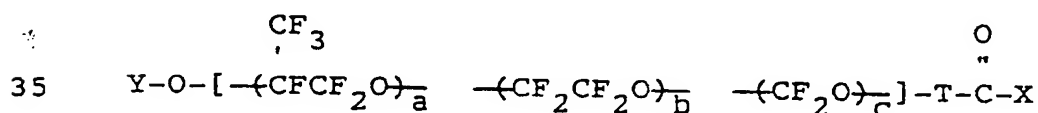weight of the peroxide is about 33,000; and
T is $-CF_2-$ and $-CF(CF_3)-$,
35   provided that when a is zero, T is not $-CF(CF_3)-$,
when b is zero T is not $-CF_2-$, and further provided
that when a and b are both zero, T is $-CF_2-$.

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It is understood that within the bracketed term
"[ ]", if more than one monomer is used, the polymer
may be a random copolymer or a block copolymer; if it
is a block copolymer, then T will be a fragment of
the last monomer used. This is also true for the
poly(perfluoroether)acyl halide percursor (infra).

Y is an end group derived from the species that
initiated the polymerization of the perfluoroether.
Most typically, and preferred, it is CF_3- when
carbonyl fluoride (COF_2) is the monomer (repeat
unit), CF_3CF_2- when tetrafluoroethylene oxide is the
monomer (repeat unit), and $CF_3CF_2CF_2-$ when
hexafluoropropylene oxide is the monomer (repeat
unit). In a random copolymer containing 2 or more of
these monomers, the end group is derived from any of
the monomers used.

It is preferred that a+b+c is a minimum of 2
and a maximum such that the molecular weight of the
peroxide does not exceed 16,500, and most preferred
that a+b+c is a minimum of 5 and a maximum such that
the molecular weight of the peroxide does not exceed
11,000. In all of the formulas in this application
a, b and c represent the average number of monomer
units in the molecule -- since the poly(perfluoro-
ether)acyl halides are made by polymerization, they
have a molecular weight distribution.

Peroxides of this formula can be prepared by
reacting a poly(perfluoroether)acyl halide with a
peroxide and a base. The poly(perfluoroether)acyl
halide is of the formula

$$Y-O-[\underset{a}{-(CFCF_2O)-} \quad \underset{b}{-(CF_2CF_2O)-} \quad \underset{c}{-(CF_2O)-}]-T-\overset{O}{\underset{\|}{C}}-X$$

with CF_3 on the first unit.

wherein

5   Y is a perfluoroalkyl group containing up to 12
     carbon atoms, a+b+c is a minimum of 2 and a
     maximum such that the maximum molecular
     weight of the acyl halide is about 16,500;

X is chlorine or fluorine; and

T is $-CF_2-$ and $-CF(CF_3)-$,

10 provided that when a is zero, T is not $-CF(CF_3)-$,
when b is zero T is not $-CF_2-$, and further provided
that when a and b are both zero, T is $-CF_2-$.

Compounds of this type are well known to those
skilled in the art, for example, U.S. Patents

15 3,250,807 and 3,347,901 and J. T. Hill, Journal of
Macromolecular Science, Chemistry, vol. A8, pages
499-520 (1974).

The base may be an alkali or alkaline earth
metal (bi)carbonate or phosphate. Such weakly basic

20 anions as carbonates and bicarbonates are preferred.
Any metal selected must provide moderate water
solubility. The molar ratio of base to acyl halide
should be at least 1.

The hydrogen peroxide may contain 16% to 90%

25 water. Thirty percent hydrogen peroxide is
preferred. The ratio of number of moles
water/peroxide is about 0.2 to about 10. The
preferred ratio is 0.8 to 6. In calculating the
ratio of water to peroxide, all water is included

30 whether introduced in the solvent or as aqueous
hydrogen peroxide. The number of moles of peroxide
(whether as hydrogen peroxide or another form) should
be approximately one-half the molar amount of the
poly(perfluoroether)acyl halide (stoichiometrically

35 equal).

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The process can be carried out in the optional presence of a solvent. Inert fluorocarbon fluids are preferred. Especially preferred is 1,1,2-trichloro-trifluoroethane.

The reaction is carried out within a temperature range chosen so that the aqueous phase will not freeze and the peroxide will not decompose. A preferred range is -30°C to 40°C. The most preferred temperature range is -15°C to 0°C.

The reaction time may vary from about 1 minute to 8 hours. Preferably the reaction time is about 5 to about 60 minutes. High speed stirring, as with a blender, increases yields.

After the reaction is complete, the reaction mixture may optionally be treated with a solid drying agent (desiccant) to remove water. Anhydrous calcium sulfate (commercially available as Drierite®) is a suitable drying agent. At the same time, it may be convenient to remove insoluble organic salts by filtration, as through glass wool.

The poly(perfluoroether)acyl peroxide may be used as a solution in the solvent in which it was made, or the solvent can be removed (at low temperature, for example by distillation under vacuum) to isolate the peroxide. As in handling peroxides in general, care should be exercised in handling the neat peroxides, especially those of relatively low molecular weight.

These poly(perfluoroether)acyl peroxides are useful as nonvolatile free radical polymerization initiators. They are also useful for preparing free radical polymerized polymers that have a perfluoroether block on one end. Such block polymers are useful for modifying the surface properties of hydrocarbon polymers, as described in European Patent Application 0,161.804.

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The poly(perfluoroether)acyl peroxides are also
useful for coating solid substrates with fluorocarbon
5   polymers. Such a process comprises:
        (1)   coating the solid substrate with a
poly(perfluoroether)acyl peroxide; and
        (2)   exposing said substrate, coated with said
peroxide, to free radical polymerizable fluorocarbon
10   monomers at a temperature at which said peroxide
decomposes to form free radicals.
        Any convenient method can be used to coat the
solid substrate with peroxide, such as dipping into,
or brushing or rolling on a solution of the peroxide,
15   and then allowing the solvent to evaporate.
Alternatively, the neat peroxide may be brushed or
rolled on. Using a solution to do the coating is
preferred. Only a minimal amount of peroxide is
needed on the solid substrate, since it acts only to
20   initiate the polymerization.
        The peroxide coated solid substrate is then
exposed to the fluorocarbon monomer at a temperature
at which the peroxide decomposes to free radicals,
about 10°C to 150°C, preferably 40°C to 80°C. The
25   fluorocarbon monomer can be gaseous, a neat liquid or
dissolved in a solvent. Obviously if another liquid
such as neat monomer or a solvent is present, the
liquid should not appreciably dissolve the peroxide.
The thickness of the coating can be controlled by the
30   ratio of surface area of the solid substrate to the
amount of fluorocarbon monomer used (area/amount of
monomer). The higher this ratio, the thinner the
coating.
        Fluorocarbon monomers suitable for the coating
35   process are those which contain at least one fluorine
atom and may be polymerized by free radicals; such

monomers are well known to those skilled in the art.
They include but are not limited to one or more of
tetrafluoroethylene, hexafluoropropylene,
perfluoro(2,2-dimethyl-1,3-dioxole), perfluoromethyl
vinyl ether, perfluoropropyl vinyl ether, vinylidene
fluoride, chlorotrifluoroethylene and vinyl fluoride
and copolymers thereof. Tetrafluoroethylene is
preferred. Small amounts, up to 10 mole percent, of
free radical polymerizable nonfluorine containing
monomers may also be copolymerized into the
fluoropolymer coating.

The substrates to be coated can be porous or
nonporous, and include, but are not limited to,
fibers, fabrics, paper, metals and ceramics.
Preferred substrates are fibers, fabrics and metals.
The substrate must be chosen so that the peroxide is
stable on the substrate. Some of the transition
metals, especially iron, may cause peroxide
decomposition and should be avoided.

In the following Examples, these symbols are
used:

A(n) is $\{CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)C(=O)O-\}_2$

B(n) is $CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)C(=O)F$

The number "n" is the average number of units in the
molecule, and is rounded off to the nearest integer.

Peroxide Titration

The peroxide titration used in the Examples
follows. In a loosely stoppered Erlenmeyer flask
several grams of dry ice are added to 25 ml of
glacial acetic acid, so as to flush oxygen from the
system. Five ml of a solution of 30 g of KI in 70 ml
of deoxygenated water is added, and then 5.0 ml of
the peroxide solution to be analyzed. The mixture is
stirred for 10 minutes to allow the peroxide to react
with the iodide. One hundred ml of deoxygenated

water is added and the deep iodine color is titrated
to light yellow with 0.1 N sodium thiosulfate. Then
5   0.5 g of "Thyodene" (from Fisher Scientific Co.)
iodometric indicator is added making the reaction
mixture turn blue. Titration is completed by
bringing to a colorless endpoint with additional
0.1 N sodium thiosulfate. Molar peroxide
10   concentration is 0.01 times the total number of ml of
sodium thiosulfate solution.

EXAMPLE 1
Preparation of A(8)
15   A flask under a positive pressure of nitrogen
was loaded with 100 ml of 1,1,2-trichlorotrifluoro-
ethane and 32 g (0.02 mole) of B(8). The mixture was
cooled to -5°C and 2.12 g of finely divided sodium
carbonate (0.02 mole) added. Next 1.0 ml of 30%
20   hydrogen peroxide (0.01 mole) was added and the
reaction mixture stirred for 3.5 hours at -5°C under
a positive pressure of nitrogen. The reaction
mxiture was passed cold through 20 g of Drierite®
(anhydrous $CaSO_4$ desiccant produced by W. A. Hammond,
25   Drierite Company), 8 mesh, in a chromatography column
which contained a plug of glass wool in the bottom.
Addition of 5.0 ml of the reaction mixture to
potassium iodide in acetic acid/water and titration
with sodium thiosulfate indicate⁻ 0.088 M peroxide.
30   With no volatile solvent loss anu 100% yield, a
peroxide concentration of 0.083 M would have been
expected.

EXAMPLE 2
Preparation of A(60)
35   A flask under a positive pressure of nitrogen
was loaded with 50 ml of 1,1,2-trichlorotrifluoro-

ethane and 102 g of B(60) (0.005 mole). The mixture
was cooled to -5°C and then 3.26 g of finely divided
5   cesium carbonate (0.01 mole) and 0.50 ml of 30%
hydrogen peroxide (0.005 mole) were added. The
mixture was stirred for 7 hours at 0°C and then
washed through 25 g of Drierite® with an additional
50 ml of 1,1,2-trichlorotrifluoroethane. This
10   mixture was stored in a -15°C refrigerator where
layer separation occurred. The upper layer titrated
for no peroxide whereas the lower layer titrated for
0.008 M peroxide. Pure peroxide of 20,000 M. W. and
density of 1.9 g/ml would be expected to titrate for
15   0.095 M peroxide.

EXAMPLE 3
Preparation of A(19)

A flask under a positive pressure of nitrogen
20   was loaded with 50 ml of 1,1,2-trichlorotrifluoro-
ethane and 34 g of B(19) (0.01 mole). The mixture
was cooled to -5°C and then 1.06 g of finely divided
sodium carbonate (0.01 mole) and 0.50 ml of 30%
hdyrogen peroxide (0.005 mole) were added. The
25   mixture was stirred for 30 minutes at -5°C and then
filtered through 50 g of Drierite® into a
polyethylene bottle. Peroxide content by titration
was 0.05 M. With no volatile solvent loss and 100%
yield, a peroxide concentration of about 0.074 M
30   would have been expected.

EXAMPLE 4
Preparation of A(21)

A Waring blender swept with nitrogen and cooled
35   in wet ice was loaded with 200 ml of 1,1,2-trichloro-
trifluoroethane, 36.9 g of B(21) (0.01 mole), and

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1.05 g of powdered sodium carbonate (0.01 mole). The
reaction was stirred briefly and then 0.5 ml of 30%
5 hydrogen peroxide (0.005 mole) added. After stirring
for 10 minutes at high speed, the reaction mixture
was filtered through 25 g of Drierite®. The filtrate
titrated 0.015 M in peroxide. With no volatile
solvent loss and 100% yield, a peroxide concentration
10 of 0.023 M would have been expected.

This Example illustrates the advantage of
efficient mixing of the water and organic phases.

EXAMPLE 5
15   Preparation of A(19)
A flask was loaded with 50 ml of 1,1,2-tri-
chlorotrifluoroethane and 34 g of B(19) (0.01 mole).
The mixture was cooled to -5°C and then 1.06 g of
finely divided sodium carbonate (0.01 mole) and
20 0.135 ml of 90% hydrogen peroxide (0.005 mole)
added. The mixture was stirred for 3.5 hours at -5°C
and then filtered through 50 g of Drierite® into a
polyethylene bottle. Peroxide content by titration
was 0.034 M. With no volatile solvent loss and 100%
25 yield, a peroxide concentration of about 0.074 M
would have been expected.

EXAMPLE 6
Preparation of Peroxide from $CF_3O(CF_2O)_3CF_2COF$
30   A flask under nitrogen was loaded with 10 g of
$CF_3O(CF_2O)_3CF_2COF$ (0.03 mole), 1.59 g of powdered
sodium carbonate (0.015 mole), and 100 ml of
1,1,2-trichlorotrifluoroethane. The mixture was
cooled to -5°C and then 1.5 ml of 30% hydrogen
35 peroxide (0.015 mole) added. The mixture was stirred
for 3 hours at -5°C and then filtered through 20 g

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of Drierite® into a polyethylene bottle. Peroxide
content by titration was 0.055 M. With no volatile
5   solvent loss and 100% yield, a peroxide concentration
of about 0.14 M would have been expected.

COMPARATIVE EXAMPLE 1
Preparation of A(7)

10   A volumetric flask loaded with 12.25 g of
sodium hydroxide was brought to 100 ml with distilled
water. This solution (33 ml) was mixed with 100 ml
of 1,1,2-trichlorotrifluoroethane and 5.2 ml of 30%
hydrogen peroxide at -5°C to -7°C. With rapid
15   stirring, 148 g of B(7) was added over 2 minutes. A
mild exotherm raised the reaction mixture to 5°C to
10°C. This mixture was stirred for another five
minutes at 0°C. The lower layer carrying a lot of
emulsified water was separated with great
20   difficulty. Shaking this layer with the usual
aqueous sodium carbonate/bicarbonate wash gave a
stiff gel. Freezing the gel and thawing, added
hundreds of ml more of 1,1,2-trichlorotrifluoro-
ethane, and forcing through Drierite® gave a small
25   quantity of 0.055 M peroxide solution.
        This Example illustrates the problems that
excessive amounts of water cause.

EXAMPLE 7
30   Coating of Aluminum with Poly(tetrafluoroethylene)
        A 0.12 M solution of A(9) in 1,1,2-trichloro-
trifluoroethane was washed down the 1.5 X 4"
rectangular face of a 16.18 g grit blasted aluminum
coupon. The coupon was dried for 15 minutes under
35   vacuum at room temperature. The coupon now weighed
16.26 g indicating A(9) pickup of 0.08 g. The coupon

was loaded into a 400 ml stainless stell autoclave
with 50 g of gaseous tetrafluoroethylene and heated
5   at 60°C for 4 hours. On recovery, the aluminum
coupon weighed 17.47 g, the 1.21 g weight gain coming
from a visually continuous plastic film of poly(tetra-
fluoroethylene) covering the grit blasted side of the
coupon.
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EXAMPLE 8
Coating of Kevlar® Fibers
with Poly(tetrafluoroethylene)
A slurry made from 4.29 g of Kevlar®
15   [poly(p-phenylterephthalamide)] fibrids, 5 ml of
0.09 M A(8), and 80 ml of 1,1,2-trichlorotri-
fluoroethane was stripped to dryness, first using a
rotary evaporator, and then a vacuum pump for fifteen
minutes. These fibrids were loaded into a 400 ml
20   autoclave with 50 g of gaseous tetrafluoroethylene.
Heating for 3 hours at 60°C gave 45.3 g of Kevlar®
fibrids coated with poly(tetrafluoroethylene).

EXAMPLE 9
25   Coating of Kevlar® Pulp with
Poly(tetrafluoroethylene/perfluoropropyl vinyl ether)
A slurry was prepared using 25 g of Kevlar®
pulp, 10 ml of 0.01 M A(9), and 250 ml of 1,1,2-
trichlorotrifluoroethane. This was stripped to
30   dryness, first using a rotary evaporator, and then a
vacuum pump for 30 minutes. The pulp was loaded into
a 400 ml autoclave along with 50 g of gaseous
tetrafluoroethylene and 3 g of gaseous
perfluoropropyl vinyl ether. Standing for 24 hours
35   at room temperature gave 51.3 g of pulp coated with
copolymer.

EXAMPLE 10

Coating of Sailcloth with Poly(tetrafluoroethylene)

5   A 3.79 g sample of polyester sailcloth was
mounted on a frame and rinsed with 1,1,2-trichloro-
trifluoroethane to clean the surface. The sailcloth
was then rinsed with 0.025 M A(10) in 1,1,2-trichloro-
fluoroethane and drained. The sample was transferred
10   to a 500 ml pressure vessel. The vessel was
evacuated for 5 minutes to remove residual 1,1,2-tri-
chlorotrifluoroethane and then pressured with 49 to
62 psi of tetrafluoroethylene gas. After standing
overnight at room temperature, the sample was
15   recovered. The cloth now weighed 6.20 g and was
covered with a shiny coating of poly(tetrafluoro-
ethylene).

        Although preferred embodiments of the invention
20   have been described, it is understood that there is
no intent to limit the invention to the precise
embodiments described and it is further understood
that the right is reserved to all changes and
modifications which fall within the scope of the
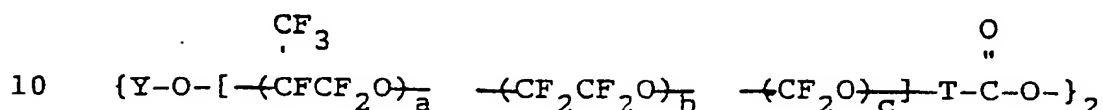25   claims.

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CLAIMS

What is claimed is:

1.   A poly(perfluoroether)acyl peroxide of the formula

$$\{Y-O-[-(CFCF_2O)_{\overline{a}} \overset{CF_3}{} \quad -(CF_2CF_2O)_{\overline{b}} \quad -(CF_2O)_{\overline{c}}]-T-\overset{O}{\overset{\|}{C}}-O-\}_2$$

wherein

Y is a perfluoroalkyl group containing up to 12

carbon atoms, $-(CFCF_2O)-$, $\overset{CF_3}{}$ $-(CF_2CF_2O)-$ and

$-(CF_2O)-$ are repeat units where a+b+c is a minimum of 2 and a maximum such that the maximum molecular weight of the peroxide is about 33,000; and

T is $-CF_2-$ and $-CF(CF_3)-$,
provided that when a is zero, T is not $-CF(CF_3)-$,
when b is zero T is not $-CF_2-$, and further provided that when a and b are zero, T is $-CF_2-$.

2.   A process for the preparation of polymeric (perfluorether)acyl peroxide product comprising reaction of an acyl halide with a peroxide, under basic conditions, in the presence of a limited amount of water, wherein the water to peroxide molar ratio is controlled in the starting reaction mixture so that such ratio is from out 0.2 to about 10.

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3.   The process of Claim 2 wherein the reaction mixture is passed through a solid desiccant to remove liquid water, at the conclusion of the reaction process.

4.   The process of Claim 3 wherein the desiccant is anhydrous calcium sulfate.

5.   The process of Claim 2 wherein the molar ratio of water to peroxide is from about 0.8 to about 6.

6.   The process of Claim 2 wherein the base is an alkali or alkaline earth (bi)carbonate or phosphate that is soluble in the reaction mixture.

7.   The process of Claim 2 carried out within a temperature range of -30°C to 40°C.

8.   The process of Claim 7 carried out within a temperature range of -15°C to 0°C.

9.   The poly(perfluoroether)acyl peroxide of Claim 1 wherein more than one type of monomer unit is enclosed within the bracketed term.

10.   The poly(perfluoroether)acyl peroxide of Claim 9 wherein the polymer is a block copolymer.

11.   The poly(perfluoroether)acyl peroxide of Claim 9 wherein the polymer is a random copolymer.

12.   The poly(perfluoroether)acyl peroxide of Claim 10 wherein "T" is a fragment of the last monomer used.

13.   The peroxide of Claim 1 wherein Y is CF_3-, a is zero, b is zero and the repeat unit is $-CF_2O-$.

14.   The peroxide of Claim 1 wherein Y is CF_3CF_2-, T is $-CF_2-$, a is zero, c is zero and the repeat unit is $-CF_2CF_2O-$.

15.   The peroxide of Claim 1 wherein Y is $CF_3CF_2CF_2-$, T is $-CF(CF_3)-$, b is zero, c is zero and the repeat unit is $-CF(CF_3)CF_2O-$.

16.   The peroxide of Claim 1 wherein the value of a+b+c is a minimum of 2 and a maximum of such that the molecular weight of the peroxide does not exceed 16,500.

17.   The peroxide of Claim 16 wherein the value of a+b+c is a minimum of 5 and a maximum such that the molecular weight of the peroxide does not exceed 11,000.

18.   The peroxide of Claim 17 wherein Y is CF_3-, a is zero, b is zero and the repeat unit is $-CF_2O-$.

19.   The peroxide of Claim 17 wherein Y is CF_3CF_2-, T is $-CF_2-$, a is zero, c is zero and the repeat unit is $-CF_2CF$ $O-$.

20.   The peroxide of Claim 17 wherein Y is $CF_3CF_2CF_2-$, T is $-CF(CF_3)-$, b is zero, c is zero and the repeat unit is $-CF(CF_3)CF_2O-$.

21.   A process for coating solid substrates
with fluoropolymers comprising:

5   (1)   coating the solid substrate with a
poly(perfluoroether)acyl peroxide, forming a coated
substrate; and

          (2)   then exposing said coated substrate to
free radical polymerizable fluorocarbon monomers at a
10   temperature at which said peroxide decomposes to form
free radicals so that said monomers are polymerized
onto said coated substrates.

22.   The process of Claim 21 wherein the
15   coating of the solid substrate is accomplished by
applying to the substrate a solution of peroxide,
then evaporating the solvent.

23.   The process of Claim 21 wherein the
20   coating of the solid substrate is accomplished by
applying neat peroxide to the substrate surface.

24.   The process of Claim 21 wherein the
temperature at which the coated substrate is exposed
25   to a free radical polymerizable fluorocarbon monomer
is about 10°C to about 150°C.

25.   The process of Claim 24 wherein the
temperature is 40°C to 80°C.
30

26.   The process of Claim 21 wherein the
fluorocarbon monomers are selected from one or more
of perfluoro(2,2-dimethyl-1,3-dioxole), perfluoro-
methyl vinyl ether, perfluoropropyl vinyl ether,
35   vinylidene fluoride, chlorotrifluoroethylene and
vinyl fluoride.

20

27.   The process of Claim 26 wherein the fluorocarbon monomer is tetrafluoroethylene.

28.   The process of Claim 21 wherein the free radical polymerizable monomers are copolymerized onto the coated substrate.

29.   The process of Claim 21 wherein the solid substrate is selected from fibers, fabrics, paper, metals and ceramics.

30.   The process of Claim 29 wherein the solid substrate is selected from fibers, fabrics and metals.

31.   The process of Claim 26 wherein the fluorocarbon monomer is gaseous.

32.   The process of Claim 26 wherein the fluorocarbon monomer is neat.

33.   The process of Claim 26 wherein the fluorocarbon monomer is in solution.

34.   The process of Claim 21 wherein the peroxide is poly(hexafluoropropylene oxide)acyl peroxide.

35.   The product of the process of Claim 21.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 07 C 409/32, C 08 G 65/32, C 08 F 4/34, C 08 F 283/06

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
IPC⁵	C 08 G, C 08 F, C 07 C

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included In the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, 11 with Indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
Y	EP, A, 0186215 (DAIKIN INDUSTRIES) 2 July 1986 see page 2, lines 19-26; page 4, line 19 - page 5, line 7; examples 1-4; claims 1-3,5	1-20
Y	FR, A, 2107356 (MINNESOTA MINING AND MANUFACTURING CO.) 5 May 1972 see page 4, line 22 - page 5, line 1; page 6, lines 29-34; example 4; claims cited in the application	1-20
A	Chemical Patents Index, Basic Abstracts Journal, Section A: PLASDOC, week 8634, 15 October 1986, AN 86-221956/34, Derwent Publications Ltd, (London, GB), & JP, A, 61152653 (DAIKIN KOGYO K.K.) 11 July 1986 see abstract	1

* Special categories of cited documents: 10

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled In the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12 octobre 1990	09. 11. 90

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	Nuria TORIBIO

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9003077
SA   38923

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 24/10/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		NL-A- 7111816	10-03-72
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